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|--|---|---|---|
| (51) International Patent Classification 5 : C09C 1/48, C08K 3/04 | | A1 | (11) International Publication Number: WO 91/13944 (43) International Publication Date: 19 September 1991 (19.09.91) |
| (21) International Application Number: | PCT/US91/01151 | | |
| (22) International Filing Date: | 21 February 1991 (21.02.91) | | |
| (30) Priority data: | 492,894 505,116 | 13 March 1990 (13.03.90) 3 April 1990 (03.04.90) | US US |
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(54) Title: IMPROVED TREADWEAR/HYSTERESIS CARBON BLACKS

(57) Abstract

Improved treadwear/hysteresis carbon blacks having a CTAB of 120-160 m²/g, a N₂SA of 120-180 m²/g, a CDBP of 95-120 cc/100 g, a DBP of 110-145 cc/100 g, a Tint/CTAB ratio of 0.80-1.10, a ΔD50 of 70-100 and a ΔD50/Dmode ratio of 0.80-1.05. Also disclosed are rubber compositions containing the carbon blacks which exhibit superior treadwear/hysteresis performance properties.

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IMPROVED TREADWEAR/HYSTERESIS CARBON BLACKS

This application is a continuation-in-part of application Serial No. 07/492,894 filed March 13, 1990.

Field of the Invention

The present invention relates to a class of new and novel furnace carbon blacks which are suitable for various applications and particularly well suited for use in rubber compositions.

Background

Carbon blacks are generally produced in a furnace-type reactor by pyrolyzing a hydrocarbon feedstock with hot combustion gases to produce combustion products containing particulate carbon black.

Carbon blacks may be utilized as pigments, fillers, reinforcing agents and for a variety of other applications. For example, carbon blacks are widely utilized as fillers and reinforcing pigments in the compounding and preparation of rubber compositions. Most importantly, carbon blacks are effective in the preparation of rubber vulcanizates intended for usage in preparing tires.

It is generally desirable in the production of tires to utilize carbon blacks which produce tires with satisfactory abrasion resistance and hysteresis performance. The treadwear properties of a tire are related to abrasion resistance. The greater the abrasion resistance of a tire, the greater the number of miles the tire will last before wearing out. The hysteresis of a rubber compound means the difference between the energy applied to deform

a rubber compound, and the energy released as the rubber compound recovers to its initial undeformed state. Tires with lower hysteresis values have reduced rolling resistance and heat build-up and therefore are able to reduce the fuel consumption of the vehicle utilizing the tire. Thus it is particularly desirable to produce carbon blacks capable of imparting greater abrasion resistance and lower hysteresis to tires. Accordingly, one object of the present invention is the production of new carbon blacks which impart improved treadwear and hysteresis performance properties to natural rubbers, synthetic rubbers and blends of natural and synthetic rubbers incorporating the carbon blacks.

Another object of the present invention is new rubber compositions, advantageous for use as truck and bus tires, incorporating the new carbon blacks.

Other objects of the present invention will become apparent from the following description and the claims.

Summary of the Invention

We have discovered new carbon blacks having a CTAB of 120-160 m²/g (square meters per gram), a nitrogen surface area (N₂SA) of 120-180 m²/g, a CDBP (crushed dibutyl phthalate number) of 95-120 cc/100g, a DBP (dibutyl phthalate number) of 110-145 cc/100g, a Tint/CTAB ratio of 0.8-1.10, a ΔD50 of 70-100 and a ΔD50/Dmode ratio of 0.80-1.05. Preferably, the carbon blacks have a CTAB of 125-150 m²/g, a N₂SA of 125-170 m²/g, a CDBP of 98-117 cc/100g, a DBP of 112-140 cc/100g, a Tint/CTAB ratio of 0.85-1.05, a ΔD50 of 72-90 and a ΔD50/Dmode ratio of 0.82-1.00. We have also discovered a new class of rubber compositions containing the carbon blacks.

The carbon blacks of the present invention may be produced in a furnace carbon black reactor having a first (combustion) zone, a transition zone, and a reaction zone. A carbon black yielding feedstock is injected in any manner known to the art, into a hot combustion gas stream. The resultant mixture of hot combustion gases and feedstock passes into the reaction zone. Pyrolysis, of the carbon black yielding feedstock, is stopped by quenching the mixture when the carbon blacks of the present invention have been formed. Preferably pyrolysis is stopped by a quench injecting a quenching fluid. The

process for preparing the novel carbon black of the present invention will be described in greater detail hereinafter.

The rubbers for which the novel carbon black of this invention are effective as reinforcing agents include natural and synthetic rubbers. Generally, amounts of the carbon black product ranging from about 10 to about 250 parts by weight can be used for each 100 parts by weight of rubber in order to impart a significant degree of reinforcement thereto. It is, however, preferred to use amounts varying from about 20 to about 100 parts by weight of carbon black per 100 parts by weight of rubber and especially preferred is the utilization of from about 40 to about 80 parts of carbon black per 100 parts of rubber.

Among the rubbers suitable for use with the present invention are natural rubber and its derivatives such as chlorinated rubber; copolymers of from about 10 to about 70 percent by weight of styrene and from about 90 to about 30 percent by weight of butadiene such as copolymer of 19 parts styrene and 81 parts butadiene, a copolymer of 30 parts styrene and 70 parts butadiene, a copolymer of 43 parts styrene and 57 parts butadiene and a copolymer of 50 parts styrene and 50 parts butadiene; polymers and copolymers of conjugated dienes such as polybutadiene, polyisoprene, polychloroprene, and the like, and copolymers of such conjugated dienes with an ethylenic group-containing monomer copolymerizable therewith such as styrene, methyl styrene, chlorostyrene, acrylonitrile, 2-vinyl-pyridine, 5-methyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine, 2-methyl-5-vinylpyridine, alkyl-substituted acrylates, vinyl ketone, methyl isopropenyl ketone, methyl vinyl ether, alphamethylene carboxylic acids and the esters and amides thereof such as acrylic acid and dialkylacrylic acid amide; also suitable for use herein are copolymers of ethylene and other high alpha olefins such as propylene, butene-1 and pentene-1; particularly preferred are the ethylene-propylene copolymers wherein the ethylene content ranges from 20 to 90 percent by weight and also the ethylene-propylene polymers which additionally contain a third monomer such as dicyclopentadiene, 1,4-hexadiene and methylene norbornene.

An advantage of the carbon black of the present invention is that the carbon blacks impart greater abrasion resistance and lower hysteresis to

compositions containing natural rubbers, synthetic rubbers or blends thereof in which the carbon blacks of the present invention are incorporated.

An advantage of the rubber compositions of the present invention is that the rubber compositions are particularly well suited for use as truck or bus tires with improved treadwear resistance and better fuel economy characteristics as compared to rubber compositions incorporating conventional, commercially available, carbon blacks.

Other advantages of the present invention will become apparent from the following more detailed description of the invention.

10 Brief Description of the Drawings:

Figure 1 is a cross-sectional view of a portion of one type of furnace carbon black reactor which may be utilized to produce the carbon blacks of the present invention.

15 Figure 2 is a graph of Rebound % versus Laboratory Abrasion Index at 7% Slip for rubber compositions produced with the carbon black of the present invention and for rubber compositions produced with reference carbon blacks.

20 Figure 3 is a graph of Rebound % versus Laboratory Abrasion Index at 14% Slip for rubber compositions produced with the carbon black of the present invention and for rubber compositions produced with reference carbon blacks.

25 Figure 4 is a graph of Rebound % versus Laboratory Abrasion Index at 21% Slip for rubber compositions produced with the carbon black of the present invention and for rubber compositions produced with reference carbon blacks.

Figure 5 is a sample histogram of the Stokes diameter of the aggregates of a carbon black sample versus the relative frequency of their occurrence in a given sample.

30 Detailed Description of the Invention:

The carbon black of the present invention is characterized by having a CTAB of 120-160 m²/g, a N₂SA of 120-180 m²/g, a CDBP of 95-120 cc/100g,

a DBP of 110-145 cc/100g, a Tint/CTAB ratio of 0.80-1.10, a ΔD_{50} of 70-100 and a $\Delta D_{50}/D_{mode}$ ratio of 0.80-1.05. Preferably, the carbon blacks have a CTAB of 125-150 m²/g, a N₂SA of 125-170 m²/g, a CDBP of 98-117 cc/100g, a DBP of 112-140 cc/100g, a Tint/CTAB ratio of 0.85-1.05, a ΔD_{50} of 72-90 and a $\Delta D_{50}/D_{mode}$ ratio of 0.82-1.00.

The carbon blacks of the present invention may be produced in a modular, also referred to as "staged", furnace carbon black reactor. A section of a typical modular furnace carbon black reactor which may be utilized to produce the carbon black of the present invention is depicted in Figure 1. Other details of a typical modular furnace carbon black reactor may be found for example in the description contained in U.S. Patent No. 3,922,335, the disclosure of which is herein incorporated by reference.

Referring to Figure 1, the carbon blacks of the present invention may be produced in a furnace carbon black reactor 2, having a combustion zone 10, which has a zone of converging diameter 11, transition zone 12, and reaction zone 18. The diameter of the combustion zone 10, up to the point where the zone of converging diameter 11, begins is shown as D-1; the diameter of zone 12, as D-2; and the diameter of zone 18, as D-3. The length of the combustion zone 10, up to the point where the zone of converging diameter 11, begins is shown as L-1; the length of the zone of converging diameter is shown as L-2; and the length of the transition zone is shown as L-3.

To produce the carbon blacks of the present invention hot combustion gases are generated in combustion zone 10, by reacting a liquid or gaseous fuel with a suitable oxidant stream such as air, oxygen, mixtures of air and oxygen or the like. Among the fuels suitable for use in reacting with the oxidant stream in combustion zone 10, to generate the hot combustion gases are included any of the readily combustible gas, vapor or liquid streams such as natural gas, hydrogen, carbon monoxide, methane, acetylene, alcohols, or kerosene. It is generally preferred, however, to utilize fuels having a high content of carbon-containing components and in particular, hydrocarbons. The ratio of air to natural gas utilized to produce the carbon blacks of the present invention may be from about 10:1 to about 20:1. To facilitate the generation

of hot combustion gases, the oxidant stream may be preheated.

The hot combustion gas stream flows downstream from zones 10 and 11 into zones 12 and then 18. The direction of the flow of hot combustion gases is shown in the figure by the arrow. Carbon black-yielding feedstock 30, is introduced at point 32 (located in zone 12). Carbon black-yielding feedstock 30, is simultaneously introduced upstream through probe 14 at point 34. The distance from the end of the zone of converging diameter 11, to point 32, is shown as F-1 and the distance from point 32 to upstream point 34 is shown as F-2. To produce the carbon black of the present invention, the feedstock may be injected in an amount of from about 40% to about 85%, by weight, at point 32, and the remainder of the total amount of from about 15% to about 60%, by weight, injected at point 34. Preferably from about 50% to about 65% of the total amount of feedstock, by weight, is introduced at point 32, and the remainder of the total amount of feedstock, from about 35% to about 50%, by weight, is introduced at point 34. In each of the examples described herein carbon black-yielding feedstock 30, was injected radially in the form of a plurality of jets which penetrate into the interior regions of the hot combustion gas stream to insure a high rate of mixing and shearing of the hot combustion gases and the carbon black-yielding feedstock so as to rapidly and completely decompose and convert the feedstock to the novel carbon black of the present invention.

The mixture of carbon black-yielding feedstock and hot combustion gases flows downstream through zone 12 into zone 18. Quench 40, located at point 42, injecting quenching fluid 50, which in Examples 1 - 4 is water, is utilized to stop pyrolysis of the carbon black-yielding feedstock when the novel carbon blacks of the present invention are formed. Point 42 may be determined in any manner known to the art, for selecting the position of a quench to stop pyrolysis. One method for determining the position of the quench to stop pyrolysis is by determining the point at which an acceptable toluene extract level for the novel carbon blacks of the present invention is achieved. Toluene extract level may be measured by using ASTM Test D1618-83 "Carbon Black Extractables - Toluene Discoloration". Q is the distance from the beginning of zone 18 to quench point 42, and will vary

according to the position of the quench.

After the mixture of hot combustion gases and carbon black-yielding feedstock is quenched, the cooled gases pass downstream into any conventional cooling and separating means whereby the carbon blacks are recovered. The separation of the carbon black from the gas stream is readily accomplished by conventional means such as a precipitator, cyclone separator or bag filter. This separation may be followed by pelletizing using, for example, a wet pelletizer.

The following testing procedures are used in the determination and evaluation of the analytical properties of the carbon blacks of the present invention, and the physical properties of the rubber compositions incorporating the carbon blacks of the present invention.

CTAB of the carbon blacks was determined according to ASTM Test Procedure D3765-85. N₂SA of the carbon blacks was determined according to ASTM D3037-88. Tinting strength (Tint) of the carbon blacks was determined according to ASTM Test Procedure D3265-85a. The CDBP (Crushed Dibutyl Phthalate) of the carbon black pellets was determined according to the procedure set forth in ASTM D 3493-86. The DBP of the carbon black pellets was determined according to the procedure set forth in ASTM D2414.

D_{mode}, and ΔD_{50} of the carbon blacks were determined in the following manner. A histogram is made of the Stokes diameter of the aggregates of the carbon black sample versus the relative frequency of their occurrence in a given sample. As shown in Figure 4, a line (B) is drawn from the peak (A) of the histogram in a direction parallel to the Y axis to and ending at the X-axis at point (C) of the histogram. The midpoint (F) of the resultant line (B) is determined and a line (G) is drawn through the midpoint (F) thereof parallel to the X-axis. Line (G) intersects the distribution curve of the histogram at two points D and E. The absolute value of the difference of the two Stokes diameters of the carbon black particles at points D and E is the ΔD_{50} value.

The data used to generate the histogram are determined by the use of a disk centrifuge such as the one manufactured by Joyce Loeb Co. Ltd. of Tyne and Wear, United Kingdom. The following procedure is a modification

of the procedure described in the instruction manual of the Joyce Loeb disk centrifuge file reference DCF 4.008 published on February 1, 1985, the teachings of which are hereby incorporated by reference, and was used in determining the data.

5 The procedure is as follows. 10 mg (milligrams) of a carbon black sample are weighed in a weighing vessel, then added to 50 cc of a solution of 10% absolute ethanol and 90% distilled water which is made 0.05% NONIDET P-40 surfactant (NONIDET P-40 is a registered trademark for a surfactant manufactured and sold by Shell Chemical Co.). The resulting suspension is dispersed by means of ultrasonic energy for 15 minutes using Sonifier Model No. W 385, manufactured and sold by Heat Systems Ultrasonics Inc., Farmingdale, New York.

10 Prior to the disk centrifuge run the following data are entered into the computer which records the data from the disk centrifuge:

- 15 1. The specific gravity of carbon black, taken as 1.86 g/cc;
2. The volume of the solution of the carbon black dispersed in a solution of water and ethanol, which in this instance is 0.5 cc.;
3. The volume of spin fluid, which in this instance is 10 cc of water;
4. The viscosity of the spin fluid, which in this instance is taken as 20 0.933 centipoise at 23 degrees C;
5. The density of the spin fluid, which in this instance is 0.9975 g/cc at 23 degrees C;
6. The disk speed, which in this instance is 8000 rpm;
7. The data sampling interval, which in this instance is 1 second.

25 The disk centrifuge is operated at 8000 rpm while the stroboscope is operating. 10 cc of distilled water are injected into the spinning disk as the spin fluid. The turbidity level is set to 0; and 1 cc of the solution of 10% absolute ethanol and 90% distilled water is injected as a buffer liquid. The cut and boost buttons of the disk centrifuge are then operated to produce a smooth concentration gradient between the spin fluid and the buffer liquid and the gradient is monitored visually. When the gradient becomes smooth such that there is no distinguishable boundary between the two fluids, 0.5 cc of the dispersed carbon black in aqueous ethanol solution is injected into the spinning

disk and data collection is started immediately. If streaming occurs the run is aborted. The disk is spun for 20 minutes following the injection of the dispersed carbon black in aqueous ethanol solution. Following the 20 minutes of spinning, the disk is stopped, the temperature of the spin fluid is measured, and the average of the temperature of the spin fluid measured at the beginning of the run and the temperature of the spin fluid measured at the end of the run is entered into the computer which records the data from the disk centrifuge. The data is analyzed according to the standard Stokes equation and is presented using the following definitions:

Carbon black aggregate - a discrete, rigid colloidal entity that is the smallest dispersible unit; it is composed of extensively coalesced particles;

Stokes diameter - the diameter of a sphere which sediments in a viscous medium in a centrifugal or gravitational field according to the Stokes equation. A non-spherical object, such as a carbon black aggregate, may also be represented in terms of the Stokes diameter if it is considered as behaving as a smooth, rigid sphere of the same density, and rate of sedimentation as the object. The customary units are expressed in nanometer diameters.

Mode (D_{mode} for reporting purposes) - The Stokes diameter at the point of the peak (Point A of Figure 2 herein) of the distribution curve for Stokes diameter.

Median Stokes diameter - (D_{st} for reporting purposes) the point on the distribution curve of Stokes diameter where 50% by weight of the sample is either larger or smaller. It therefore represents the median value of the determination.

The Shore A Hardness of the rubber compositions was determined according to the procedure set forth in ASTM D-2240-86.

The abrasion data of the rubber compositions were determined using an abrader which is based on a Lambourn type machine. Abrasion rates (cubic centimeter/centimeter travel) were measured at 7%, 13% and 21% slip. The slip is based on the relative velocity of the plates rather than angle of slip. In the following examples, the abrasion index is the ratio of the abrasion rate of a control composition containing VULCAN 6 carbon black, a trademarked product of Cabot Corporation, Waltham, Massachusetts divided by the abrasion

rate of a composition produced using a specified carbon black of the present invention, at the same slip.

The modulus, tensile and elongation of the rubber compositions were measured by the procedure set forth in ASTM D412.

Rebound data were determined on all rubber samples utilizing a ZWICK Rebound Resilience Tester, Model 5109, manufactured by Zwick of America, Inc., Post Office Box 997, East Windsor, Connecticut 06088. Instructions for determining the rebound values accompany the instrument.

The effectiveness and advantages of the present invention will be further illustrated by the following examples.

EXAMPLES 1-4

Four examples of the novel carbon blacks of the present invention were prepared in a reactor generally described herein, and as depicted in Figure 1, utilizing the reactor conditions and geometry set forth in Table I. The fuel utilized in the combustion reaction in each of the examples was natural gas. The liquid feedstock utilized in each of the examples had the properties indicated in the chart below:

Feedstock Properties

| | |
|---|-------|
| Hydrogen/Carbon Ratio | 0.93 |
| Hydrogen (wt.%) | 7.16 |
| Carbon (wt.%) | 91.2 |
| Sulfur (wt.%) | 0.4 |
| A.P.I. Gravity 15.5/15.6 C(60)F [ASTM D-287] | -2.2 |
| Specific Gravity 15.5/15.6 C(60)F [ASTM D-287] | 1.094 |
| Viscosity, SUS (54.4°C) [ASTM D-88] | 105.8 |
| Viscosity, SUS (98.9°C) [ASTM D-88] | 40.8 |
| BMCI (Visc-Grav) | 135 |

The reactor conditions and geometry are set forth in Table I below.

TABLE I

| | | CARBON BLACKS | | | |
|----|---|---------------|---------------|---------------|---------------|
| | | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 4 |
| 5 | D-1, in. | 7.25 | 7.25 | 7.25 | 7.25 |
| | D-2, in. | 5.3 | 5.3 | 5.3 | 5.3 |
| | D-3, in. | 9 | 9 | 9 | 9 |
| | L-1, in. | 24 | 24 | 24 | 24 |
| 10 | L-2, in. | 12 | 12 | 12 | 12 |
| | L-3, in. | 11.5 | 11.5 | 11.5 | 11.5 |
| | F-1, in. | 5.75 | 5.75 | 5.75 | 5.75 |
| | F-2, in. | 26 | 26 | 26 | 26 |
| | Q, in. | 38 | 26 | 26 | 32 |
| 15 | Oil Inj Pt. 32,) 6 x Tips # x Size, in.) 0.031 | 6 x 0.0225 | 6 x 0.0225 | 6 x 0.0225 | 6 x 0.0225 |
| | Oil Rate 32, gph 93 | 94 | 85 | 94 | |
| | Oil Press. 32, psig 217 | 493 | 402 | 430 | |
| | Oil Preheat, 32, °F 126 | 338 | 337 | 332 | |
| 20 | Oil Inj. Pt. 34,) 3 x Tips # x Size, in.) 0.070 | 3 x 0.070 | 3 x 0.070 | 3 x 0.070 | 3 x 0.070 |
| | Oil Rate 34, gph 46 | 46 | 43 | 47 | |
| | Oil Press. 34, psig 35 | 30 | 26 | 27 | |
| | Oil Preheat 34, °F 224 | 267 | 256 | 257 | |
| 25 | Comb.Air, kscfh 115 | 115 | 115 | 115 | 115 |
| | Comb.Air Preheat, °F 900 | 900 | 900 | 900 | 900 |
| | Natural Gas, kscfh 9.7 | 9.7 | 9.7 | 9.7 | 9.7 |
| | Air/Burn Gas Ratio 9.9 | 9.9 | 9.9 | 9.9 | 9.9 |
| | K+, gK+/100gal oil 1.5 | 6.3 | 2.1 | 5.3 | |
| 30 | Quench Press., psi 350 | 140 | 260 | 170 | |
| | Temp. at Quench, °F 1350 | 1350 | 1350 | 1350 | |

Inj. = Injection; Comb. = combustion; Press. = pressure

32 = Point 32 on Figure 1; 34 = Point 34 on Figure 1;

gph = gallons/hour; psi=pounds/square inch; in.= inches;
ft.= feet; °F = degrees Fahrenheit; kscfh = standard cubic
feet/hour, in 1000's

K+ = potassium; gK+/100gal oil = grams K+/100 gallons
feedstock (oil)

The carbon blacks produced in Examples 1-4 were then analyzed according
40 to the procedures described herein. The analytical properties of the blacks
produced, after wet pelletizing and drying, and two reference carbon blacks
were as follows:

| | | | | | Carbon Black | | |
|----|---------------------------------------|-------|-------|-------|--------------|----------|------------|
| | | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 4 | VULCAN 6 | VULCAN 10H |
| | CTAB (m ² /g) | 131 | 129 | 149 | 135 | 109 | 135 |
| 5 | N ₂ SA (m ² /g) | 141 | 133 | 159 | 156 | 111 | 140 |
| | DBP (cc/100g) | 118 | 114 | 128 | 115 | 114 | 127 |
| | CDBP (cc/100g) | 104 | 100 | 110 | 102 | 98 | 102 |
| | Tint (%) | 132 | 132 | 131 | 135 | 114 | 132 |
| | Tint/CTAB | 1.01 | 1.02 | 0.88 | 1.00 | 1.04 | 0.98 |
| | Dmode | 90 | 86 | 90 | 84 | 89 | 73 |
| 10 | Δ D50 | 86 | 78 | 82 | 74 | 62 | 60 |
| | Δ D50/Dmode | 0.96 | 0.91 | 0.87 | 0.84 | 0.70 | 0.82 |

VULCAN 6 carbon black and VULCAN 10H carbon black are trademarked carbon blacks manufactured and sold by Cabot Corporation, Waltham, Massachusetts.

15 Example 5

This Example illustrates the use of the novel carbon blacks of the present invention in rubber compositions in comparison with rubber compositions produced using, VULCAN 6 carbon black and VULCAN 10H carbon black. Rubber composition A was made with the carbon black of the present invention produced in Example 1. Rubber composition A was made with the carbon black of the present invention produced in Example 1. Rubber composition B was made with the carbon black of the present invention produced in Example 2. Rubber composition C was made with the carbon black of the present invention produced in Example 3. Rubber composition D was made with the carbon black of the present invention produced in Example 4. Rubber composition E was made with VULCAN 6 carbon black. Rubber composition F was made with VULCAN 10H carbon black. Rubber compositions A, B, C, D, E and F were prepared incorporating each of the carbon black samples according to the rubber formulation procedure shown below in Table II.

TABLE II

| | INGREDIENT | Part by weight |
|----|--|----------------|
| 5 | Natural Rubber | 100 |
| | Carbon Black | 50.00 |
| | Zinc Oxide | 5.00 |
| | Circo Light Rubber Process Oil | 5.00 |
| | Stearic Acid | 3.00 |
| 10 | Sunproof Improved | 2.50 |
| | Santoflex 13 | 1.5 |
| | AgeRite Resin D | 1.5 |
| | Santocure MOR | 1.2 |
| | Sulfur | 1.8 |
| 15 | Circo Light Rubber Process Oil is a naphthenic oil, ASTM D2226, Type 103; Sunproof Improved is a mixture of waxy materials used as a stabilizer; Santoflex 13 is n-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene-diamine; AgeRite Resin D is polymerized 1,2-dihydro-2,2,4 trimethylquinoline; Santocure MOR is 2(Morpholinothio) benzothiazole. | |
| 20 | | |

The static properties of these rubber compositions were then evaluated according to the ASTM procedures described herein. The results were as follows:

| | Rubber Composition | Modulus 300% El (psi) | Tensile (psi) | El _b * (%) | Shore A Hardness |
|----|--------------------|-----------------------------|------------------|--------------------------|---------------------|
| 25 | A | 1514 | 3832 | 571 | 65 |
| | B | 1834 | 4176 | 556 | 58 |
| 30 | C | 1946 | 4229 | 568 | 59 |
| | D | 1911 | 4515 | 566 | 57 |
| | E | 1591 | 3882 | 567 | 60 |
| | F | 1503 | 4017 | 610 | 67 |

35 *El_b = elongation at break; psi = pounds/square inch

These results show that the static properties of the rubber compositions A, B, C and D produced with the carbon blacks of the present invention are comparable to those of rubber compositions E and F produced with reference carbon blacks.

40 The Laboratory Abrasion Index and Rebound % of each rubber composition were also evaluated as described herein. The results were as follows:

| Rubber Composition | 7% Slip | 13% Slip | 21% Slip | Rebound % |
|--------------------|---------|----------|----------|-----------|
| A | 128.4 | 123.3 | 101 | 47.4 |
| B | 122.1 | 136.2 | 119.4 | 48.7 |
| C | 121.5 | 123.6 | 116.1 | 46.1 |
| D | 116.1 | 129.3 | 143.2 | 47.1 |
| E | 100 | 100 | 100 | 53.7 |
| F | 116.7 | 106.0 | 95.9 | 46.5 |

5 The laboratory abrasion index data show that rubber compositions A, B, C and D, containing the carbon blacks of the present invention, exhibit improved abrasion resistance/hysteresis performance properties compared with rubber compositions E and F incorporating the control carbon blacks. The improved abrasion/hysteresis performance properties of the rubber compositions containing the carbon blacks of the present invention, at 7%, 13% and 21%
10 slip values are depicted graphically in Figures 2, 3 and 4.

15 It should be clearly understood that the forms of the present invention herein described are illustrative only and are not intended to limit the scope of the invention.

WHAT IS CLAIMED IS:

1 1. A carbon black having a CTAB of 120-160 m²/g, a N₂SA of 120-180
2 m²/g, a CDBP of 95-120 cc/100g, a DBP of 110-145 cc/100g, a Tint/CTAB
3 ratio of 0.80-1.10, a ΔD50 of 70-100 and a Δ D50/Dmode ratio of 0.80-1.05.

1 2. The carbon black of claim 1 wherein the CTAB is 125-150 m²/g, the
2 N₂SA is 125-170 m²/g, the CDBP is 98-117 cc/100g, the DBP is 112-140
3 cc/100g, the Tint/CTAB ratio is 0.85-1.05, the ΔD50 is 72-90 and the
4 ΔD50/Dmode ratio is 0.82-1.00.

1 3. The carbon black of claim 1 wherein the CTAB is 131 m²/g, the N₂SA
2 is 141 m²/g, the CDBP is 104 cc/100g, the DBP is 118 cc/100g, the
3 Tint/CTAB ratio is 1.01, the ΔD50 is 86 and the ΔD50/Dmode ratio is 0.96.

1 4. The carbon black of claim 1 wherein the CTAB is 129 m²/g, the N₂SA
2 is 133 m²/g, the CDBP is 100 cc/100g, the DBP is 114 cc/100g, the
3 Tint/CTAB ratio is 1.02, the ΔD50 is 78 and the ΔD50/Dmode ratio is 0.91.

1 5. The carbon black of claim 1 wherein the CTAB is 149 m²/g, the N₂SA
2 is 159 m²/g, the CDBP is 110 cc/100g, the DBP is 108 cc/100g, the
3 Tint/CTAB ratio is 0.88, the ΔD50 is 82 and the ΔD50/Dmode ratio is 0.87.

1 6. The carbon black of claim 1 wherein the CTAB is 135 m²/g, the N₂SA
2 is 156 m²/g, the CDBP is 102 cc/100g, the DBP is 115 cc/100g, the
3 Tint/CTAB ratio is 1.00, the ΔD50 is 74 and the ΔD50/Dmode ratio is 0.84.

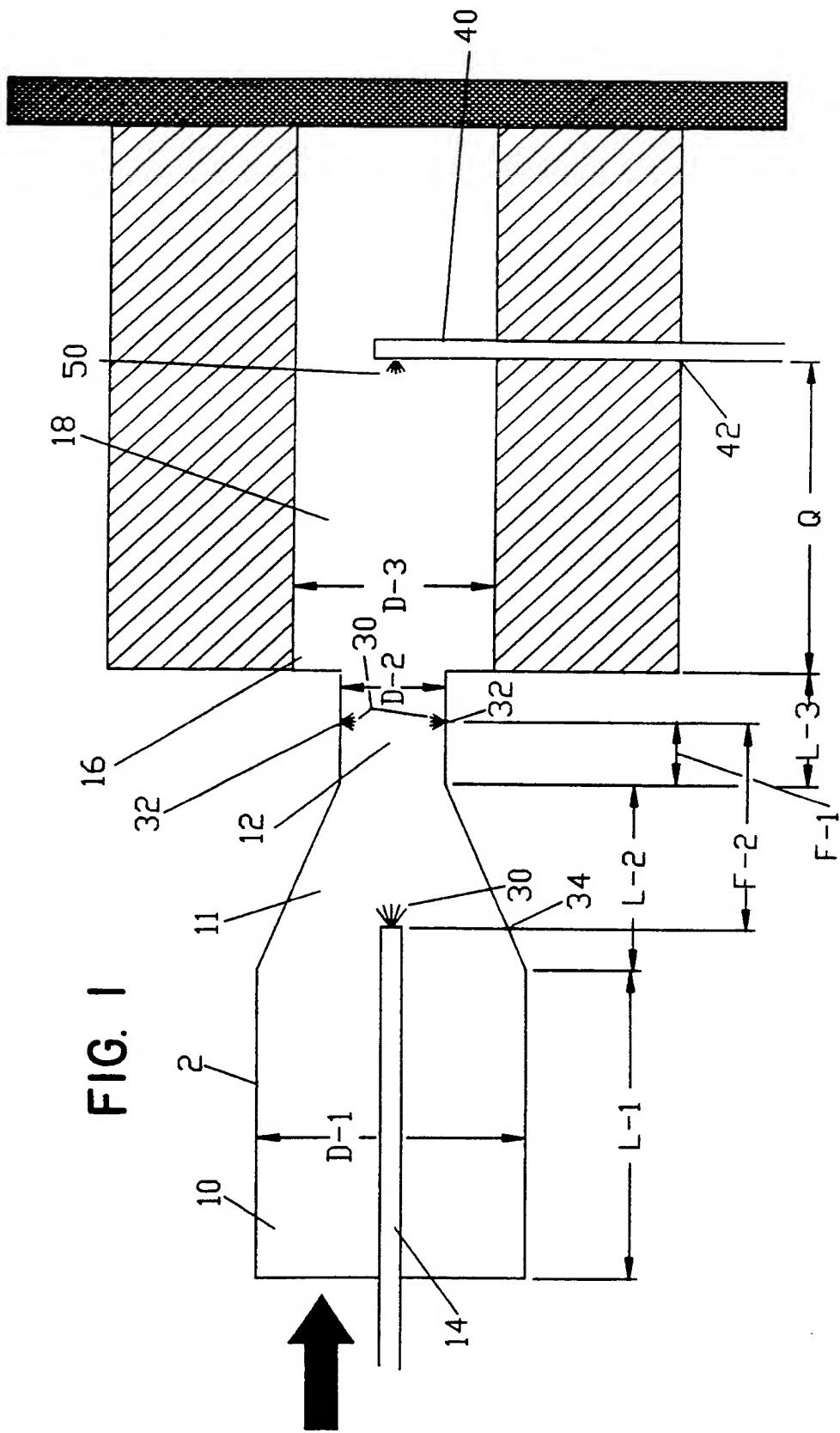
1 7. A rubber composition comprising about 100 parts, by weight, of a rubber
2 and from about 10 to about 250 parts, by weight, of a carbon black having a
3 CTAB of 120-160 m²/g, a N₂SA of 120-180 m²/g, a CDBP of 95-120 cc/100g,
4 a DBP of 110-145 cc/100g, a Tint/CTAB ratio of 0.80-1.10, a ΔD50 of 70-
5 100 and a Δ D50/Dmode ratio of 0.80-1.05

1 8. The rubber composition of claim 7 wherein the CTAB of the carbon
2 black is 125-150 m²/g, the N₂SA of the carbon black is 125-170 m²/g, the
3 CDBP of the carbon black is 98-117 cc/100g, the DBP of the carbon black is
4 112-140 cc/100g, the Tint/CTAB ratio of the carbon black is 0.85-1.05, the
5 ΔD_{50} of the carbon black is 72-90 and the $\Delta D_{50}/D_{mode}$ ratio of the carbon
6 black is 0.82-1.00.

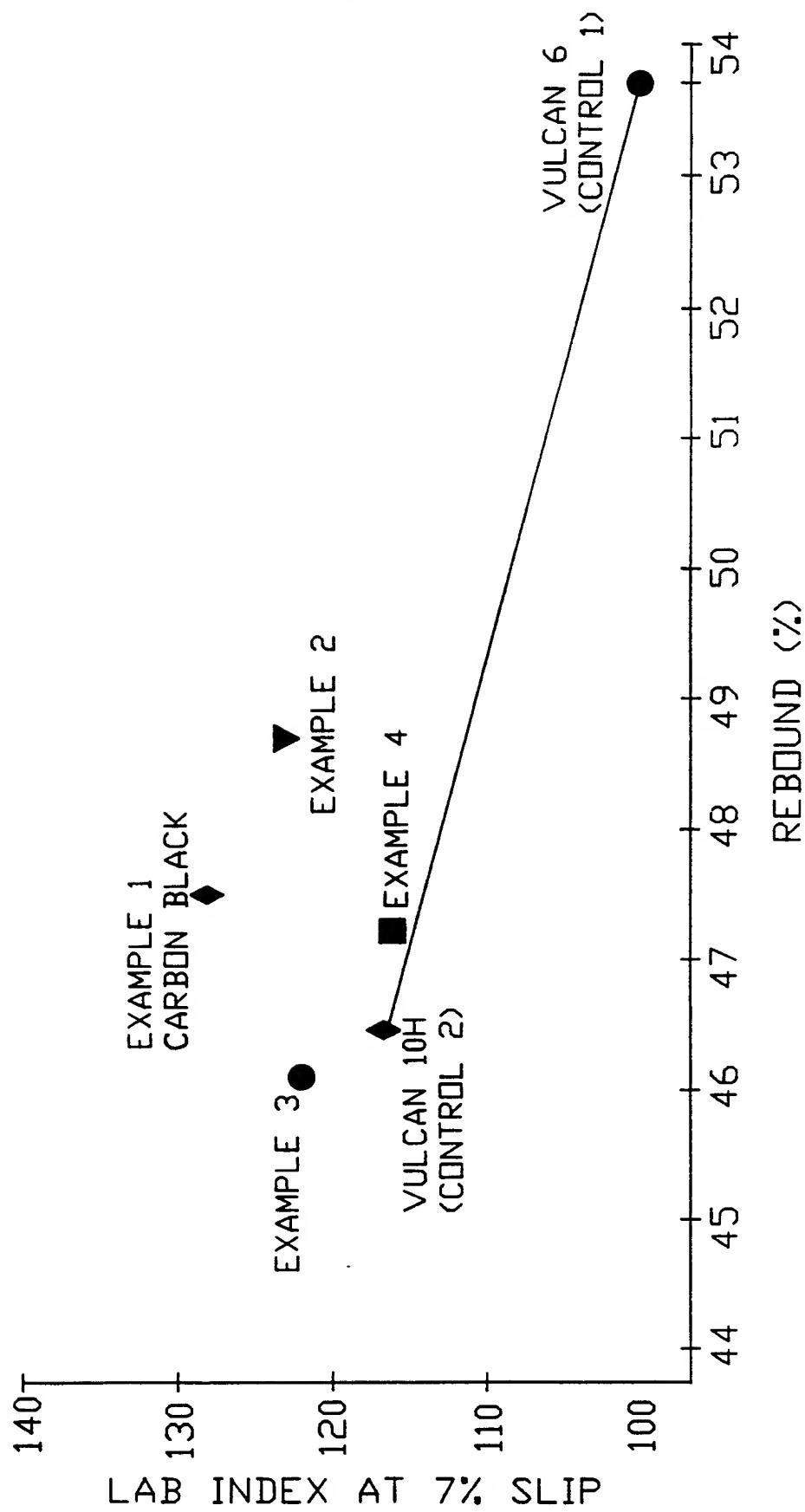
1 9. The rubber composition of claim 7 wherein the rubber is natural rubber.

1 10. The rubber composition of claim 7 wherein the carbon black is present in
2 an amount of from about 50 to about 100 parts, by weight, per 100 parts, by
3 weight rubber.

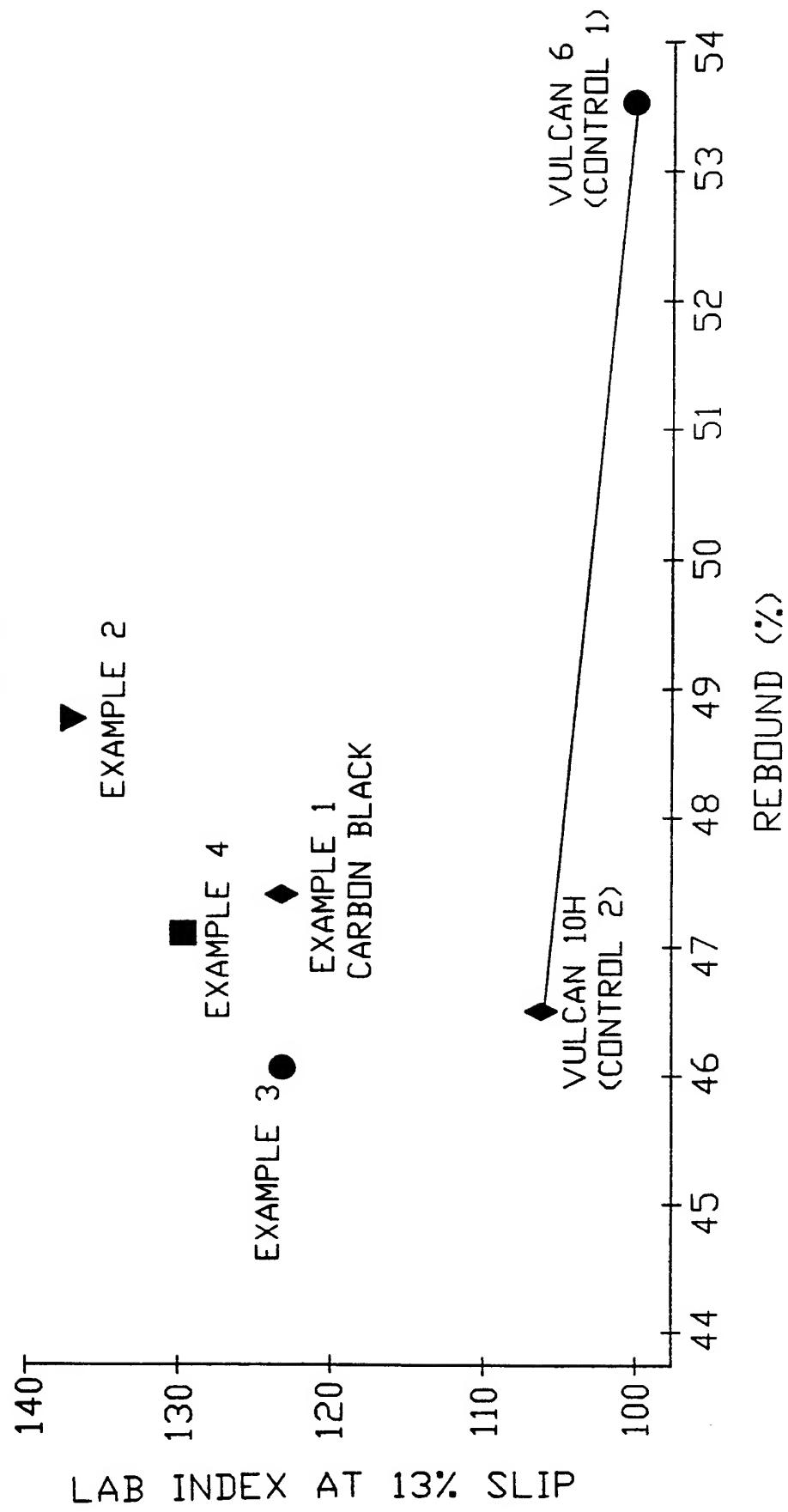
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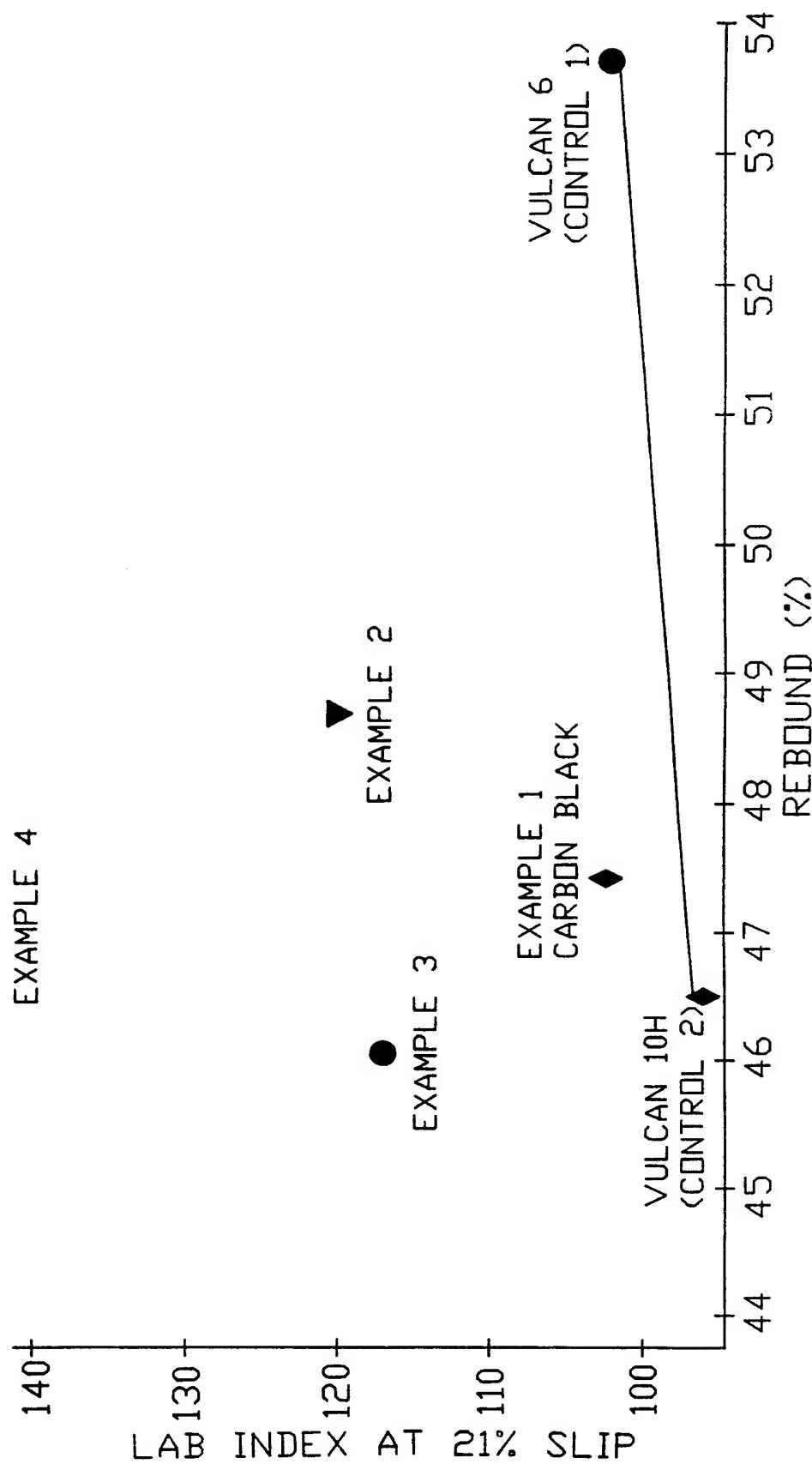
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FIG. 2

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FIG. 3

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FIG. 4

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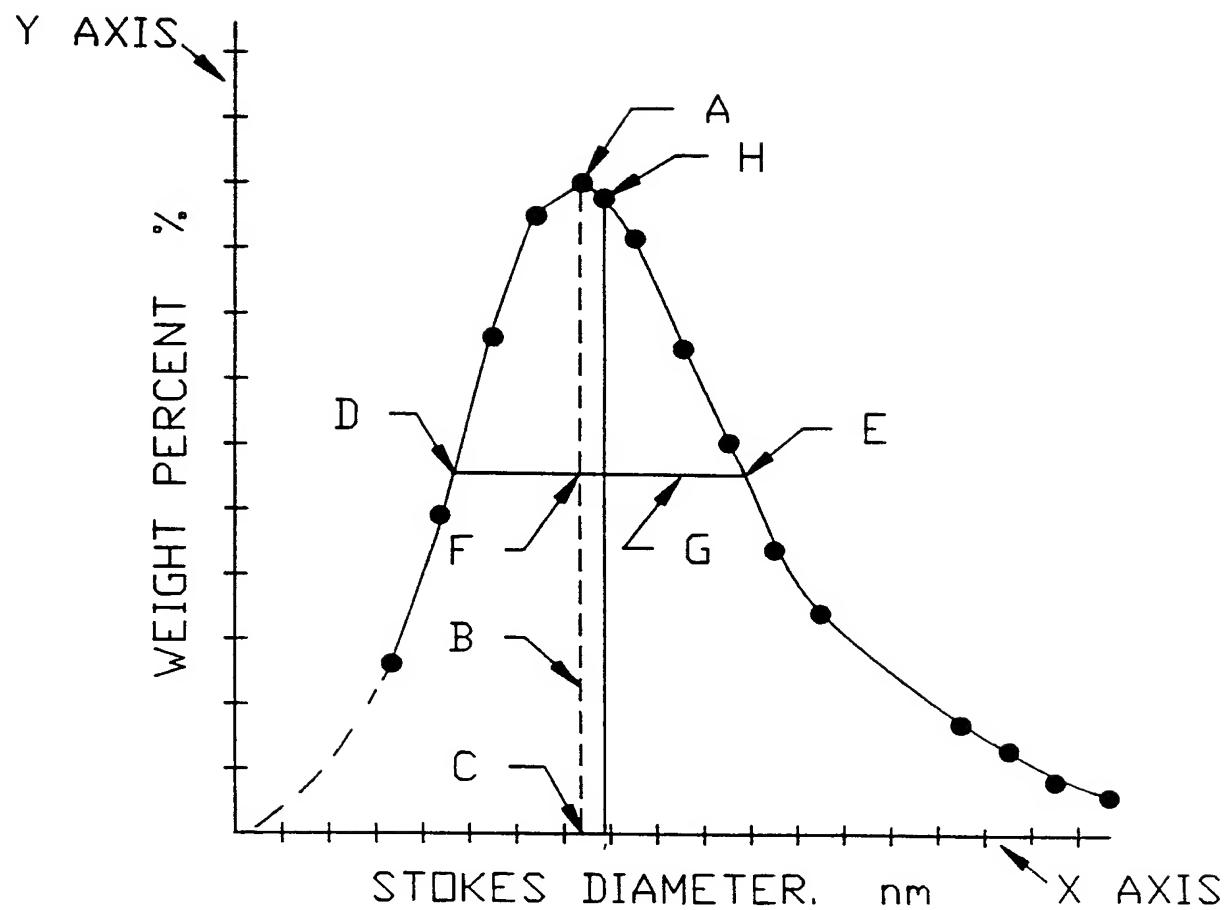


FIG. 5

INTERNATIONAL SEARCH REPORT

PCT/US91/01151

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC. (5): C09C 1/48; C08K 3/04

U.S. CL 423/445; 524/495, 496

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

| Classification System | Classification Symbols |
|---|------------------------|
| U.S. | 423/445; 524/495, 496 |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵ | |

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

| Category ⁶ | Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁶ | Relevant to Claim No. ¹⁷ |
|-----------------------|--|-------------------------------------|
| X | JP, A, 62-290738 (BRIDGESTONE TIRE KK) 17 DECEMBER 1987; See entire document. | 1-10 |
| Y | US, A, 4,703,079 (AHMAD) 27 OCTOBER 1987; See entire document. | 1-10 |

• Special categories of cited documents: ¹⁸

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

| Date of the Actual Completion of the International Search ¹⁹ | Date of Mailing of this International Search Report ²⁰ |
|---|---|
| 23 APRIL 1991 | 17 MAY 1991 |
| International Searching Authority ²¹ ISA/US | Signature of Authorized Officer ²⁰ Edward J. Cain Edward J. Cain |